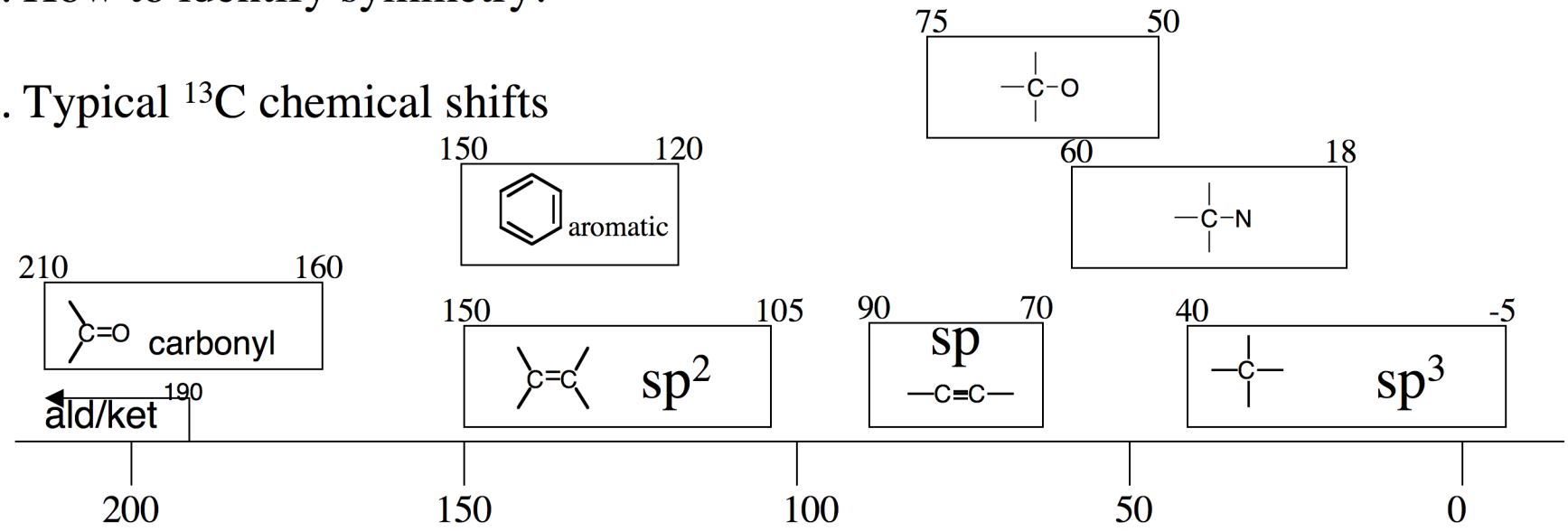
You Should Know:

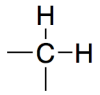
1. IHD = $\frac{2N+2 - (\#\text{hydrogens+halogens}) + (\#Ns)}{2}$; where N is number of C's

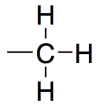
2. How to identify symmetry.

3. Typical ^{13}C chemical shifts



3. Multiplicities

(s) singlet (t) triplet 

(d) doublet (q) quartet 

4. Proton Inventory: Identify if any protons are attached to non carbon atoms by summing number of C-attached protons and comparing to molecular formula.

Table 5.2 The ^{13}C Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

Compound	C-1	C-2	C-3	C-4	C-5
Methane	−2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH_3)	

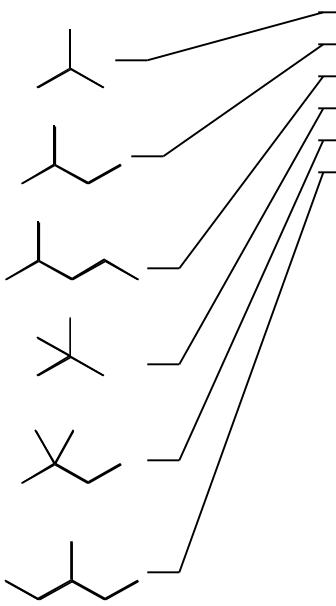
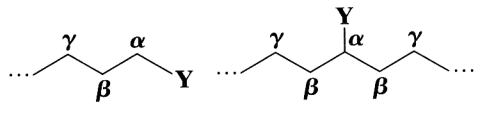


Table 5.3 Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal[a] (+ left, − right)



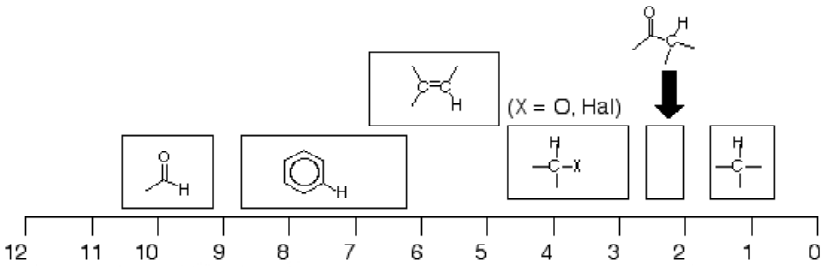
Terminal Internal

	α		β		γ
Y	Terminal	Internal	Terminal	Internal	
CH_3	+ 9	+ 6	+10	+ 8	−2
$CH{=}CH_2$	+20		+ 6		−0.5
$C{\equiv}CH$	+ 4.5		+ 5.5		−3.5
COOH	+21	+16	+ 3	+ 2	−2
COO^-	+25	+20	+ 5	+ 3	−2
COOR	+20	+17	+ 3	+ 2	−2
COCl	+33	+28		+ 2	
$CONH_2$	+22		+ 2.5		−0.5
COR	+30	+24	+ 1	+ 1	−2
CHO	+31		0		−2
Phenyl	+23	+17	+ 9	+ 7	−2
OH	+48	+41	+10	+ 8	−5
OR	+58	+51	+ 8	+ 5	−4
OCOR	+51	+45	+ 6	+ 5	−3
NH_2	+29	+24	+11	+10	−5
NH_3^+	+26	+24	+ 8	+ 6	−5
NHR	+37	+31	+ 8	+ 6	−4
NR_2	+42		+ 6		−3
NR_3^+	+31		+ 5		−7
NO_2	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	−3
SH	+11	+11	+12	+11	−4
SR	+20		+ 7		−3
F	+68	+63	+ 9	+ 6	−4
Cl	+31	+32	+11	+10	−4
Br	+20	+25	+11	+10	−3
I	− 6	+ 4	+11	+12	−1

[a] Add these increments to the shift values of the appropriate carbon atom in Table 5.2 or to the shift value calculated from Table 5.1.

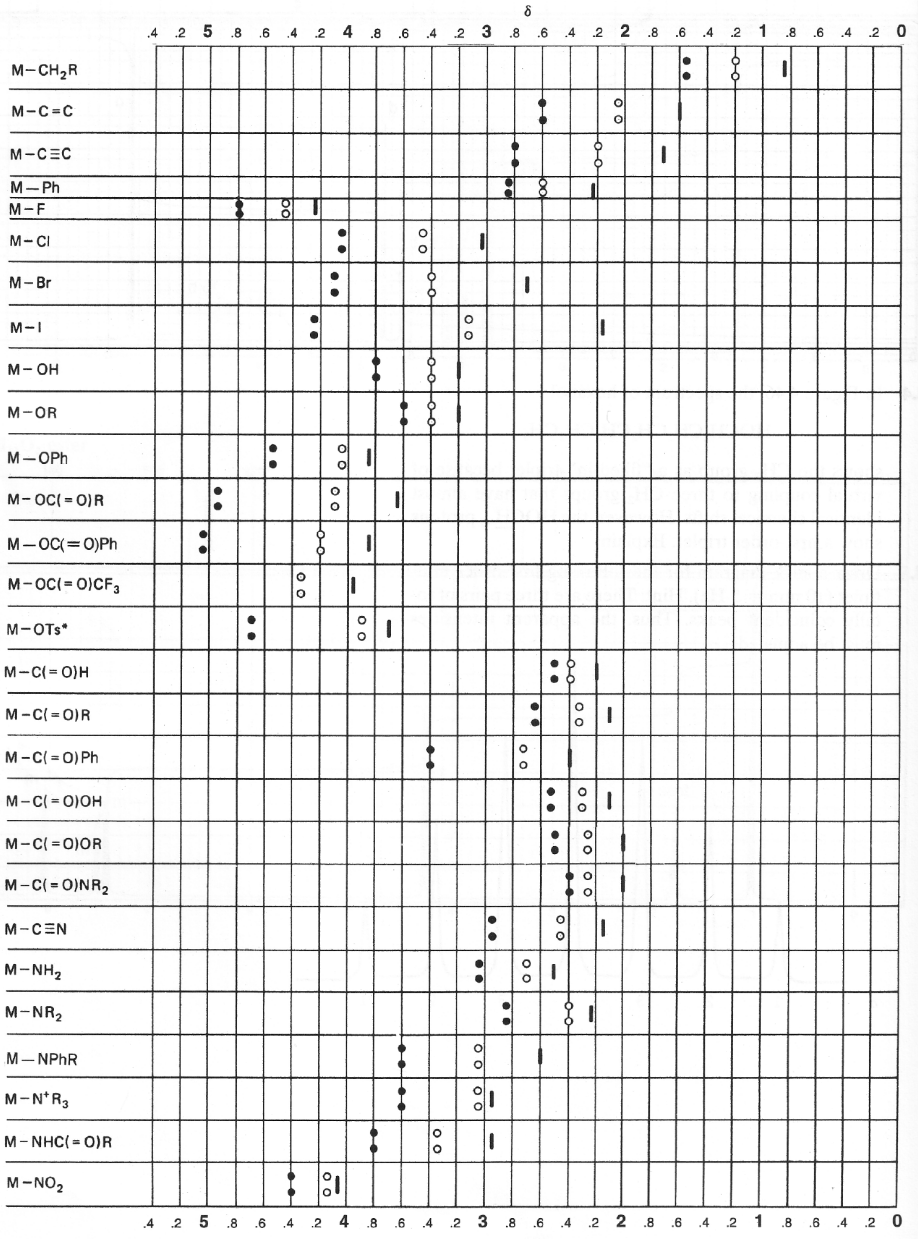
Source: Wehrli, F.W., Marchand, A.P., and Wehrli, S. (1983). *Interpretation of Carbon-13 NMR Spectra,* 2nd ed. London: Heyden.

Down Field *Up Field*



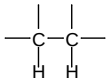
Appendix A CHART A.1 Chemical Shifts of Protons on a Carbon Atom Adjacent (α Position) to a Functional Group in Aliphatic Compounds (M—Y)

▮ M = methyl
▮ M = methylene
⋮ M = methine



Coupling Constants Depends on Structure and Geometry

Approximate Coupling Constants.

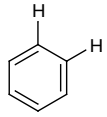


7 Hz
(free rotation)

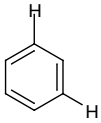
10 Hz

15 Hz

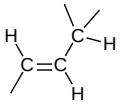
2 Hz



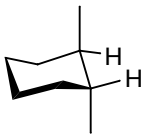
8 Hz



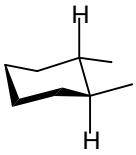
2 Hz



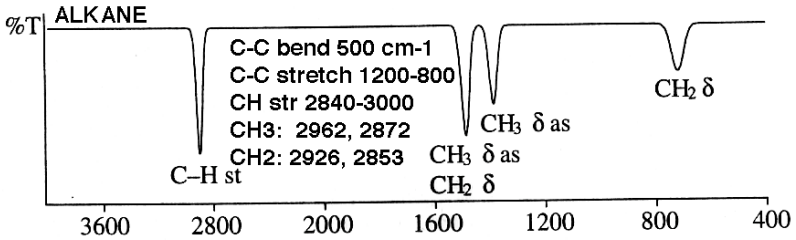
6 Hz

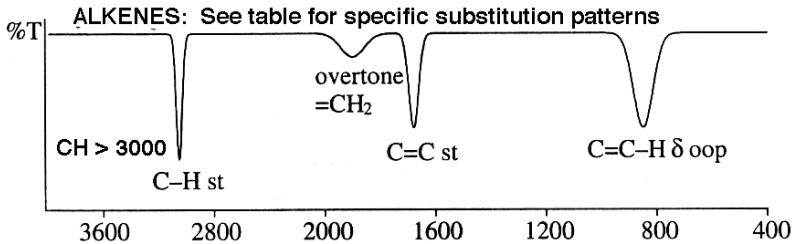


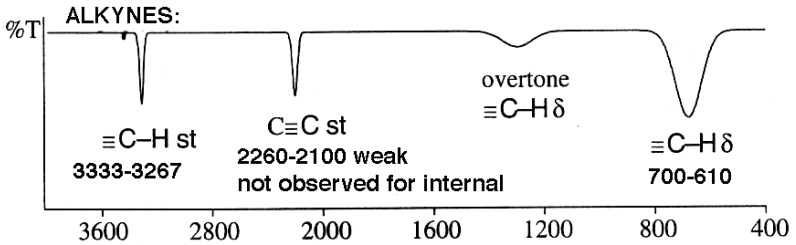
J = 2-3 Hz

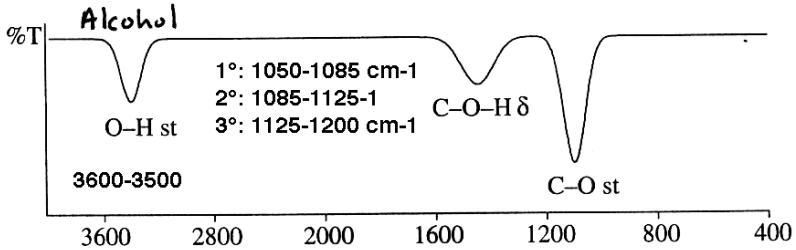


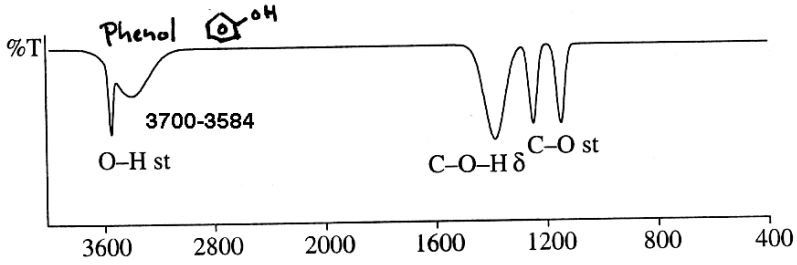
J = 8-10 Hz



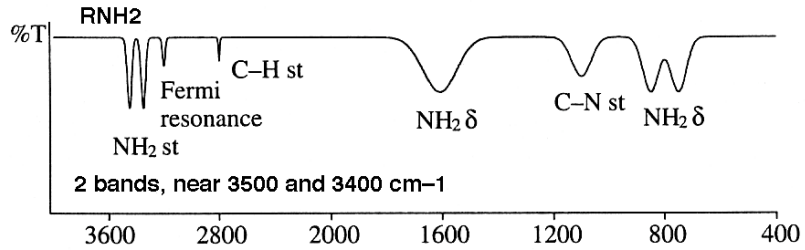




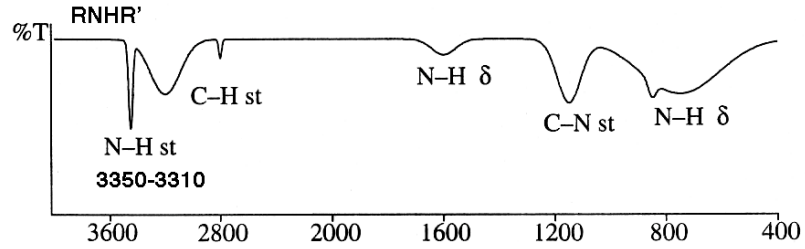




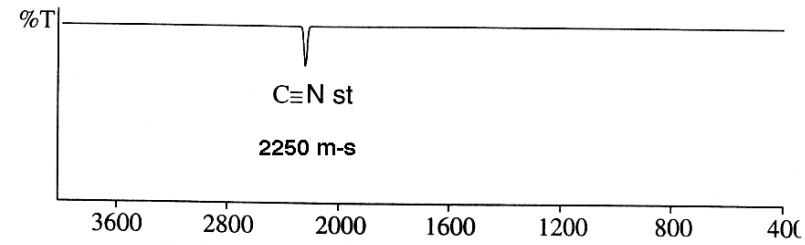
Primary Amines



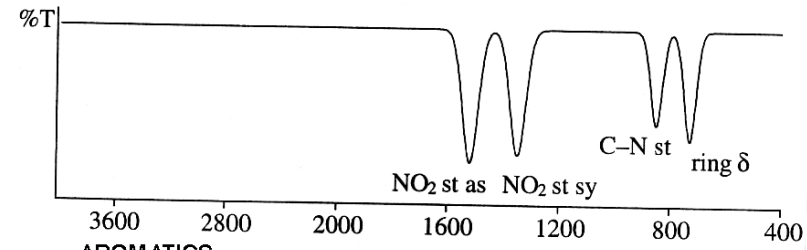
Secondary Amines

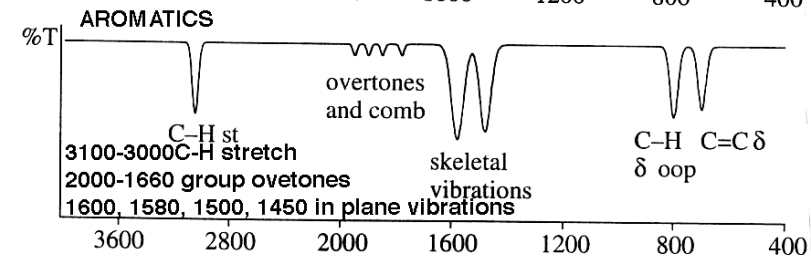


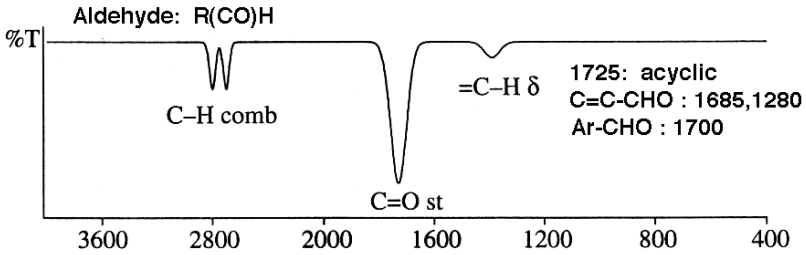
Nitriles

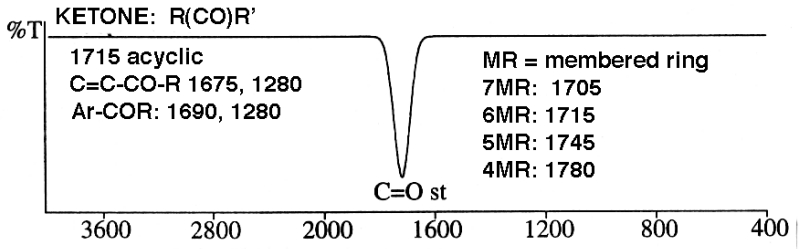


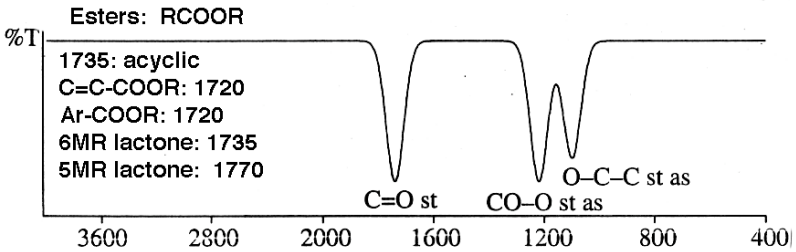
Nitro Compounds



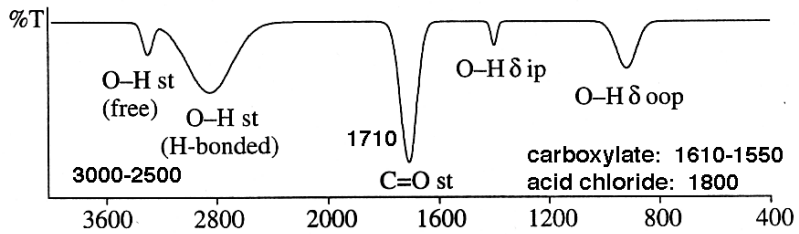


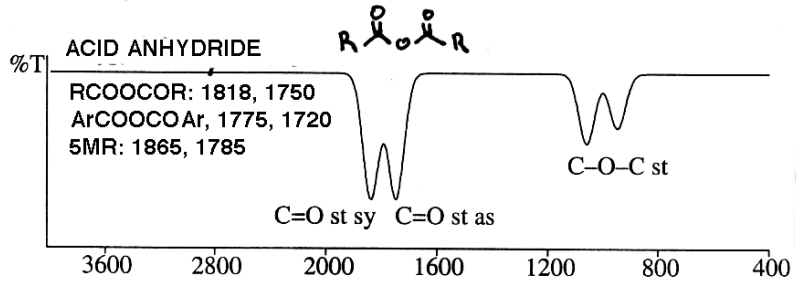




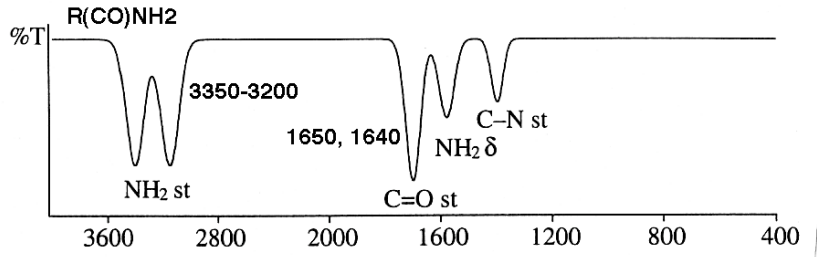


Carboxylic Acids

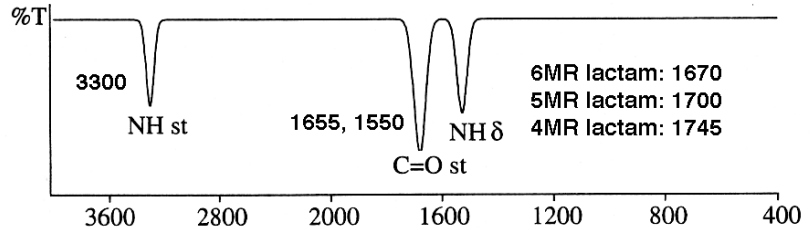




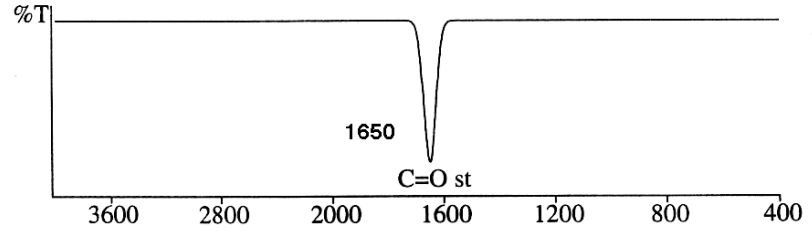
Primary Amides



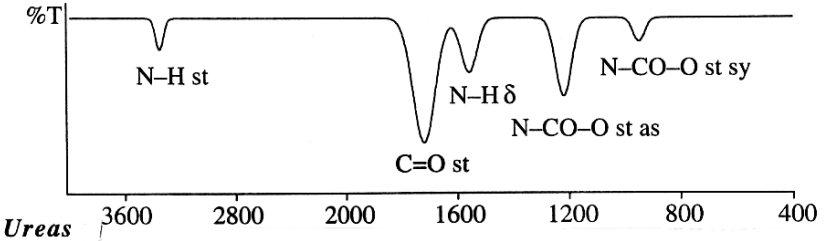
Secondary Amides



Tertiary Amides



Carbamates



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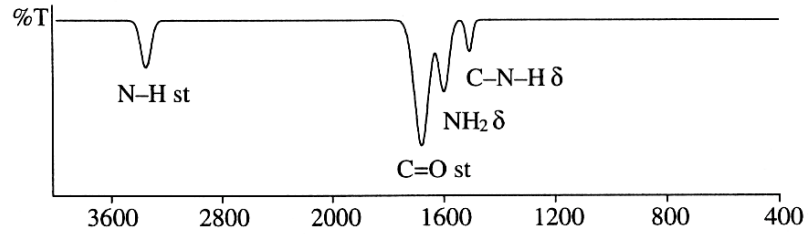
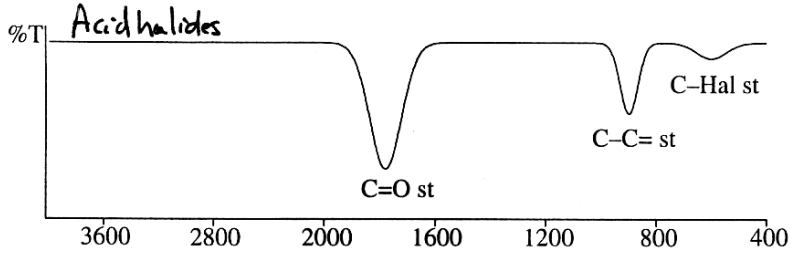
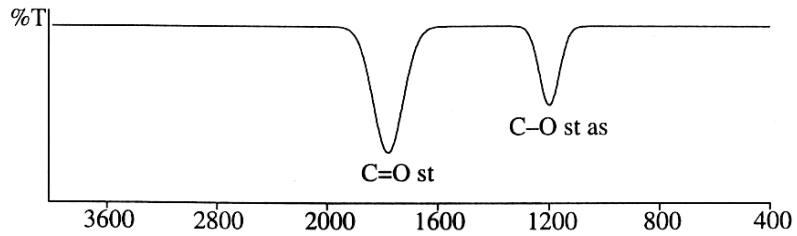
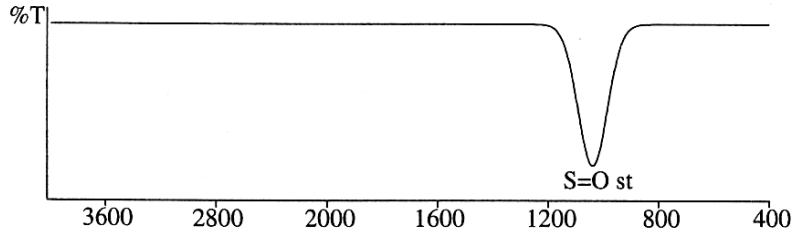




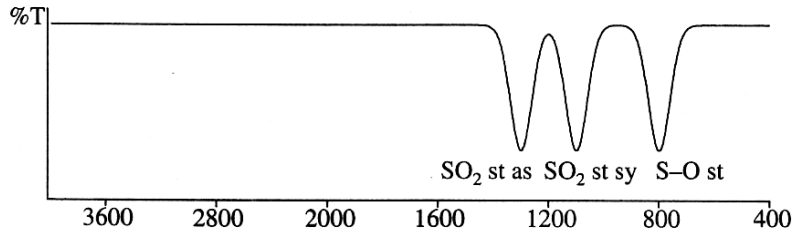
Carbonic Acid Derivatives



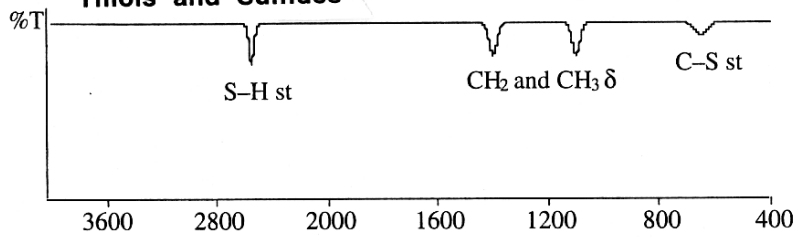
Sulfoxides



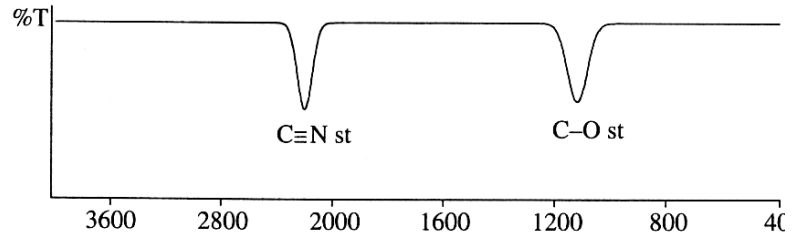
Sulfones



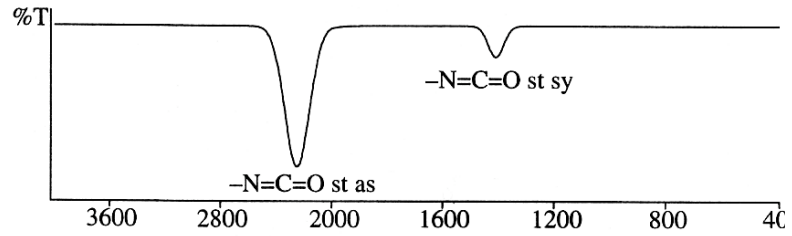
Thiols and Sulfides



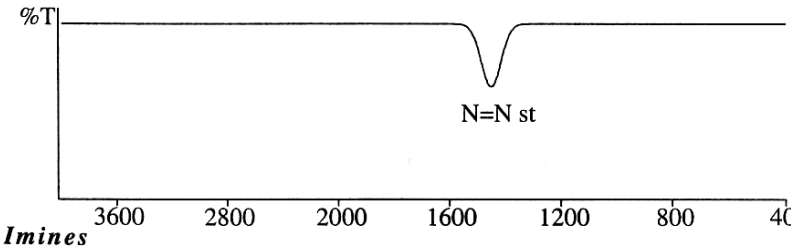
Cyanates



Isocyanates



Azo Compounds



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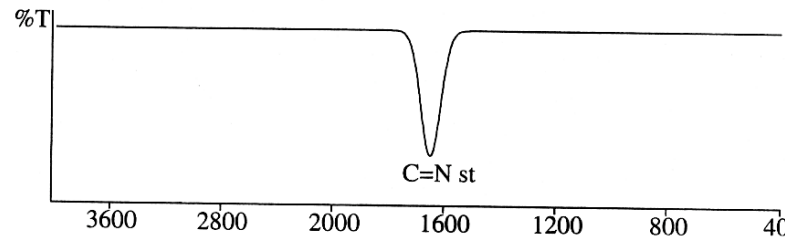
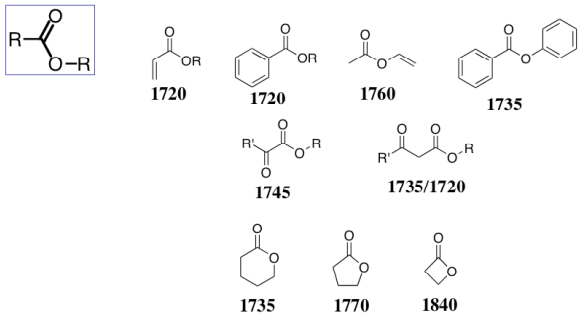


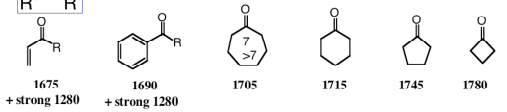
Ester: 1735 + two at 1300-1050



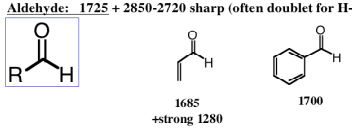
Carbonyl Compounds: 1870-1600 cm^{-1} (strong absorbance)

Ketone: 1715

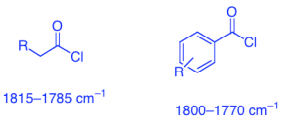
1240-1100: strong in aliphatic ketones
1280: strong in aromatic or α, β unsaturated ketones



Aldehyde: 1725 + 2850-2720 sharp (often doublet for H-CO)

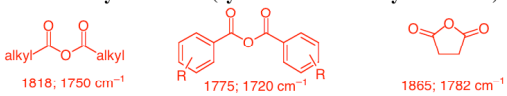


Acid Halides



Anhydrides

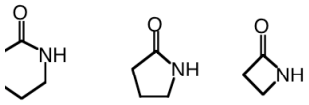
- **Two carbonyl stretches (symmetrical and asymmetrical)**

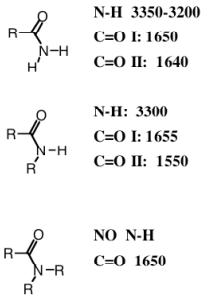


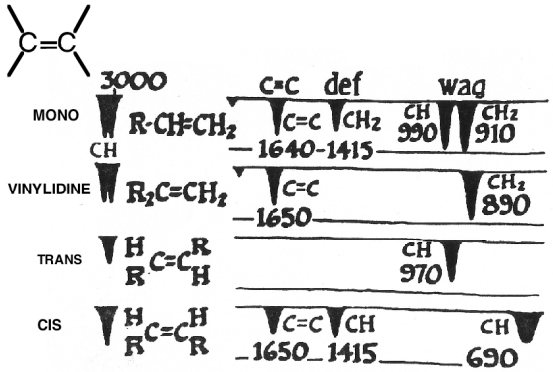
1650

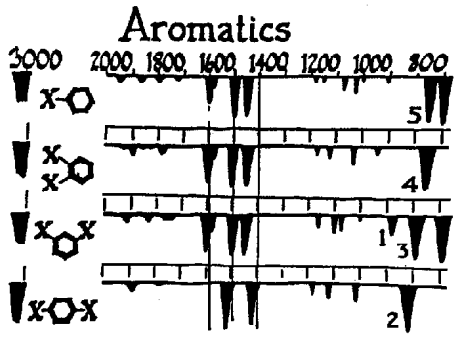
Amide: ~~1705~~ #### + two at 1300-1050

Coupling between C=O stretch and N-H gives double peak









3100-3000C-H stretch and overtones
2000-1660 group ow week ovetones
1600, 1580, 1500, 1450 in plane vibrations (not seen with all substitutions)

Alcohols:

R–O–H RO-H 3640-3600 sharp if not hydrogen bonded/solvated
3600-3500 m hydrogen bonded or solvated
C-OH 1° = 1050, 2° = 1100, 3° = 1150

—C≡N (nitrile) 2250 m-s

—C≡C–H Alkyne C≡C-H 3300 strong and sharp
—C≡C–R - C≡C- 2260-2190 very weak or absent

R–O–R Ethers C-O-C 1150-1070 s

Nitro: 1660-1500(s) asymmetrical stretch
390-1260(s) symmetrical stretch

Amines

- NH stretching
  - in dilute solution, primary amines (RNH_2) display 2 bands, near 3500 and 3400 cm^{-1}. These represent 'free' asymmetrical and symmetrical stretches.
  - in dilute soln, secondary amines (R_2NH) display one band near 3350-3310 cm^{-1}.
  - weaker and sharper than OH

  - neat primary aliphatic amines (alkylNH_2) absorb at 3400-3300 and 3330-3250 cm^{-1}. ArylNH_2 absorb at slightly higher frequencies.

Alkynes

- —C≡C— stretch: weak absorption at 2260-2100 cm^{-1}
  - not observed for symmetrical alkynes (v. weak for 'pseudo' symmetric alkynes
  - terminal alkynes (R-C≡C-H) absorptions are stronger than internal (R-C≡ C-R) absorptions

- C≡C–H stretch:
  - 3333–3267 cm^{-1}
  - strong, narrow (as compared to OH or NH)

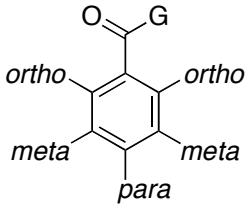
- C≡C–H bend:
  - 700-610 cm^{-1}: broad, strong absorption
  - 1400-1220 cm^{-1}, overtone of above

UV-VIS Calculation Tables

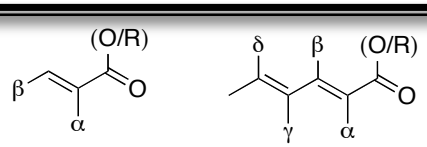
Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
$N(Alk)_2$	+60
Solvent correction[b]	+0
λ_{calc} = Total	

[a]See L. M. Fieser and M. Fieser, *Steroids*. New York: Reinhold, 1959, pp. 15–24; R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942); A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. New York: Pergamon (Macmillan), 1964.

[b]Solvents have negligible effects upon the λ_{max} of these $\pi \rightarrow \pi^*$ transitions.



ArCOR/ArCHO/$ArCO_2H$/$ArCO_2R$		λ_{max}^{EtOH} (nm)
Parent chromophore: Ar = C_6H_5		
G = Alkyl or ring residue, (e.g., ArCOR)		246
G = H, (ArCHO)		250
G = OH, OAlk, ($ArCO_2H$ and $ArCO_2R$)		230
Increment for each substituent on Ar:		
—Alkyl or ring residue	o-, m-	+3
	p-	+10
—OH, —OCH_3, —OAlk	o-, m-	+7
	p-	+25
—O^- (oxyanion)	o-	+11
	m-	+20
	p-	+78[b]
—Cl	o-, m-	+0
	p-	+10
—Br	o-, m-	+2
	p-	+15
—NH_2	o-, m-	+13
	p-	+58
—$NHCOCH_3$	o-, m-	+20
	p-	+45
—$NHCH_3$	p-	+73
—$N(CH_3)_2$	o-, m-	+20
	p-	+85



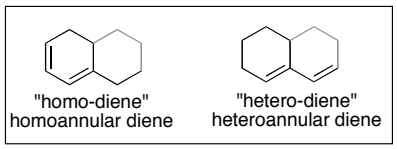
enone dienone

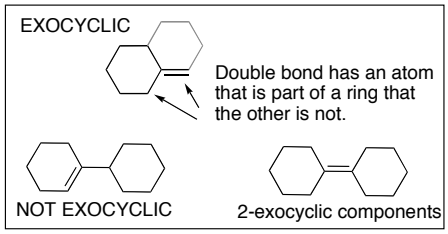
Base values		(nm)
Acyclic α,β-unsaturated ketones		215
Six-membered cyclic α,β-unsaturated ketones		215
Five-membered cyclic α,β-unsaturated ketones		202
α,β-Unsaturated aldehydes		210
α,β-Unsaturated carboxylic acids and esters		195
Increments for		
Double bond extending conjugation		+30
Alkyl group, ring residue	α	+10
	β	+12
	γ and higher	+18
Polar groupings: —OH	α	+35
	β	+30
	δ	+50
—OAc	α,β,δ	+ 6
—OMe	α	+35
	β	+30
	γ	+17
	δ	+31
—SAlk	β	+85
—Cl	α	+15
	β	+12
—Br	α	+25
	β	+30
$—NR_2$	β	+95
Exocyclic double bond		+5
Homodiene component[a]		+39
Solvent correction (see table below)		Variable
λ_{calc} = Total[b]		

[a]Two conjugated double bonds, both in the same ring.

[b]The calculated values usually fall within ±3 nm of the observed values. The molar absorptivities of *cisoid* enones are usually less than 10,000, whereas the molar absorptivities of *transoid* enones are greater than 10,000.

Terminology

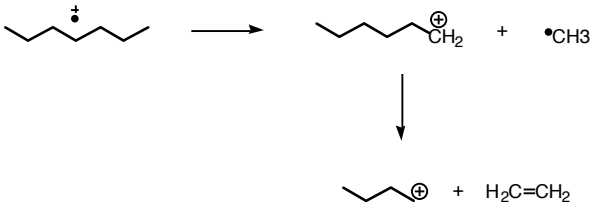




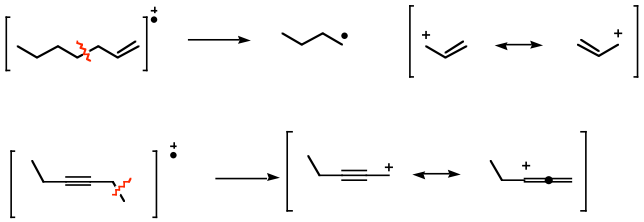
J. Koh --adapted from Silverstein and Webster "Spectrocopic Identification of Organic Compounds, Wiley , 1998.

Alkanes

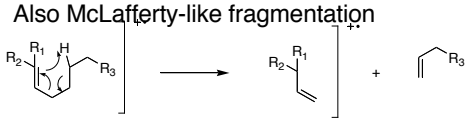
Fragmentation tends to favor more stable carbocation
Remember: you only see the charged fragment in the MS.



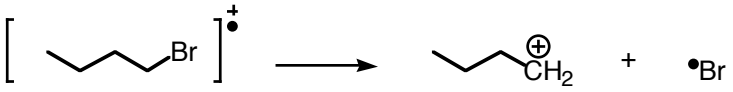
Alkenes/Alkynes



Also McLafferty-like fragmentation

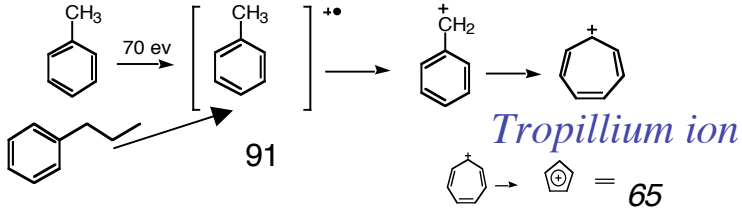


Halides:



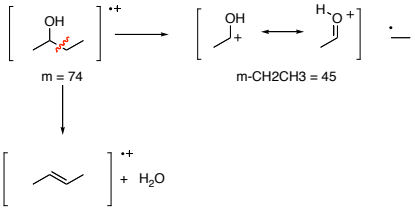
Note: unique isotopic ratio of most halides!

Aromatic:



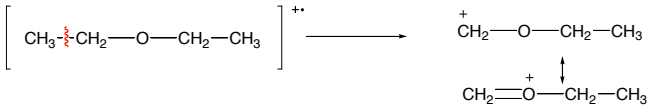
Alcohols

Note: molecular ion is often weakor absent.
alpha cleavage and dehydration are common fragmentations

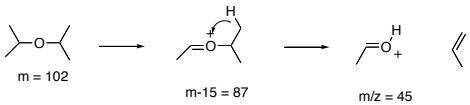


ROR Ethers

Notes: molecular ion is often weak
alpha cleavage a are common fragmentations

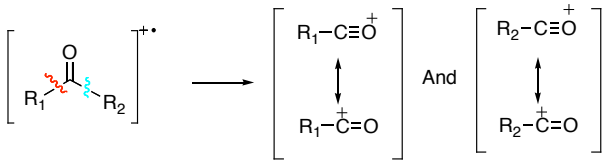


Ethers with branched alpha carbons tend to undergo secondary fragmentation

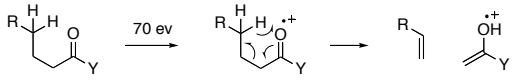


Carbonyls:

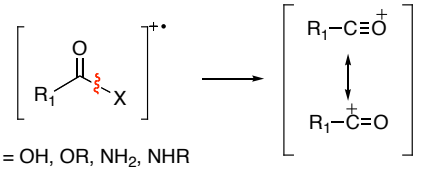
Ketones and Aldehydes /Esters, Acids,Amides:
Major Fragmentation pattern is alhpa cleavage resulting in loss of side-chain and formation of acylium inon



Also McLafferty Rearrangement where possible!



must have gamma proton



X = OH, OR, NH_2, NHR

note:

$HO-C\equiv O^+$ m/z = 45

$H_2N-C\equiv O^+$ m/z = 44